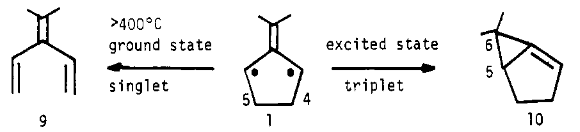
undergo secondary photolysis. However, as was established by light-filtering experiments, this pathway would require that the absorption spectrum of **10** extend toward the red as far as 315 nm.

Bicyclic hydrocarbon **4** is already known[16] to be a minor product (15–20%) of the photolysis of diazene **3** at 77 K, where it probably arises from ring closure of the short-lived singlet state of biradical **1**. Compound **4** also seems to be formed in the present experiments as a photolysis product of triplet **1**, but it cannot be a source of the other monomeric hydrocarbons under these conditions because it has only end absorption in the ultraviolet region, and is photochemically stable to 3000-Å radiation.

A parallel study[12] shows that the thermally produced (presumably singlet) intermediate **1** uses the internal energy it has acquired at 400 °C for the exothermic destruction of the $C_4$–$C_5$ bond. In contrast, the photochemically excited triplet **1** generated here uses its ~90 kcal/mol of excitation energy to stitch up a weak C–C bond ($C_5$–$C_6$ of **10** and probably $C_1$–$C_4$ of **4**), a reaction that would be endothermic[17] in the ground state.



**Acknowledgment.** We thank the National Science Foundation (CHE-8011399) and the National Institutes of Health (GM-23375) for support of this work. We also thank the National Science Foundation (CHE 7916210) for its support of the NSF Northeast Regional NMR Facility at Yale University. Acknowledgement is made to the donors of the Petroleum Research Fund, sponsored by the American Chemical Society, for partial support of this work. Dr. R. F. Salinaro made a helpful contribution in an early phase of this project.

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(16) (a) Rule, M.; Lazzara, M. G.; Berson, J. A. *J. Am. Chem. Soc.* **1979**, *101*, 7091. (b) Rule, M.; Mondo, J. A.; Berson, J. A. *Ibid.* **1982**, *104*, 2209.

(17) Mazur, M. R.; Berson, J. A. *J. Am. Chem. Soc.* **1982**, *104*, 2217.

# High-Temperature Pathways on the Energy Surface Connecting a Vinylidene and a Trimethylenemethane. Gas-Phase Generation of a Bicyclo[3.1.0]hex-1-ene and a Novel Cyclization of a 1,2,5-Triene

Mark R. Mazur,[1] Stephen E. Potter,[2] Allan R. Pinhas, and Jerome A. Berson*

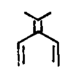
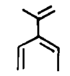
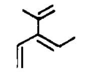
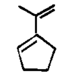
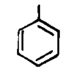
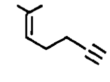
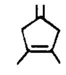
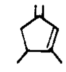
*Department of Chemistry, Yale University*
*New Haven, Connecticut 06511*

*Received July 15, 1982*

Although the thermal chemistry of the trimethylenemethane biradical **1** at moderate temperatures is almost entirely intermolecular (dimerization or cycloaddition with olefins),[3] we have found a richly detailed set of novel intramolecular transformations at higher temperature.

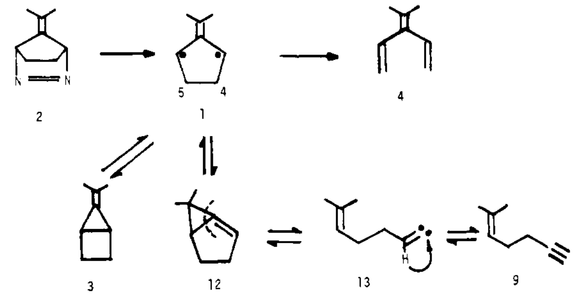
Flash vacuum pyrolysis of the diazene **2** at temperatures above 400 °C and pressures of $10^{-3}$–$10^{-4}$ torr gave the products shown in Table I. Control experiments established the occurrence of the reactions **4** → **5** + **6** (+**7**?); **5** ⇌ **6**; **5**, **6**, or **7** → **4**; **5** or **6** → **4**; and **7** → **4**–**6**. These processes were slow enough to permit the identification of the primary pyrolysis products as **4** and **7**–**9**.

Table I. Products of Flash Vacuum Pyrolysis[b] of Diazene **2** and Eneyne **9**[a-c]

| product | | % yield from reactant | |
|---|---|---|---|
| | | diazene 2 | enyne 9 |
| 4 |  | 10 | 31 |
| 5 |  | 25 | 10 |
| 6 |  | 30 | 10 |
| 7 |  | 5 | 1 |
| 8 |  | 10 | 32 |
| 9 |  | 1 | |
| 10 |  | 0 | 6 |
| 11[d] |  | 0 | b |

[a] At 700 °C, $10^{-3}$–$10^{-4}$ torr, residence time ~0.02 s. [b] Experimental details given in supplementary material. [c] Unless otherwise noted, all products were identified by isolation. [d] Identified by gas chromatographic retention time.

Scheme I



Scheme I shows proposed mechanisms for the formation of **4** and **9**, in which no attempt is made to decide the extremely subtle question of whether the actual pathways originate from the biradical **1** or the bicyclic hydrocarbon **3**.

The enyne **9** apparently arises by a route beginning with cyclization of **1** to the bicyclo[3.1.0]hex-1-ene **12**. This compound suffers *thermal* vinylidene cycloreversion to the carbene **13**, which then undergoes a well-documented[4] type of hydrogen shift. The possibility that the **12** → **9** reaction may be concerted cannot be evaluated on the basis of the present experiments.

Reversal of the entire cyclization sequence was observed in the pyrolysis of the enyne **9** (Table I), which gave the same group of trienes **4**–**6** obtained from diazene **2**. Another major product from **9** was toluene (**8**), which also was observed from diazene **2**, probably as a secondary product via **9**. The formation of **8** can be rationalized by several mechanisms which we have not yet been able to distinguish experimentally.

Products **10** and **11**, although superficially seeming to resemble

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(1) Humphrey Chemical Co. Fellow, 1981–1982.

(2) Harkness Fellow of the Commonwealth Fund, 1973–1975.

(3) (a) Berson, J. A. *Acc. Chem. Res.* **1978**, *11*, 446. (b) Berson, J. A. In "Diradicals"; Borden, W. T. Ed.; Wiley-Interscience: New York, 1982.

(4) Brown, R. F. C.; Harrington, K. J. *J.* Chem. *Soc.*, *Chem. Commun.* **1972**, 1175 et seq.

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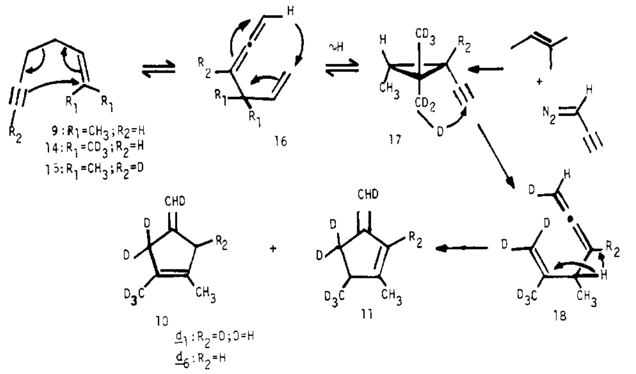
Scheme II



the methylenecyclopentenes found and plausibly rationalized by Huntsman[5] in the pyrolyses of certain 1-en-5-ynes or their valency tautomeric eneallenes (1,2,5-trienes), in fact are structurally different in a crucial sense. They are formed by a novel multistep mechanism (Scheme II), involving Cope rearrangement, two successive hydrogen shifts, and ring closure by either of two formal intramolecular ene reactions.

Two separate isotope-position-labeling experiments were carried out. Pyrolysis at 700 °C of —C≡C—D labeled enyne **15** gave product **10**-$d_1$ with the label exclusively at the ring methylene position ($^2$H NMR absorption at $\delta$ 3.02). The same treatment of $(CD_3)_2C{=}C <$ labeled enyne **14** gave **10** with one exocyclic methylene deuteron ($\delta$ 4.91), two ring methylene deuterons, and three methyl deuterons ($\delta$ 1.63). Evidently, one of the two methyl groups of the reactant **14** does not survive intact in the product **10**-$d_6$. In addition to a rationalization of the labeling patterns, the mechanism[6,7] of Scheme II predicts that pyrolysis of the proposed cyclopropane intermediate **17** should give **10**. This prediction was confirmed by the independent synthesis of a mixture of **17** and its trans stereoisomer (from 3-diazopropyne and 2-methyl-2-butene), which upon pyrolysis gave >95% of an approximately equimolar mixture of **10** and **11**, each identified by isolation and independent synthesis.

Scheme I and Table I show that the dominant thermal reaction of the TMM **1** is cleavage of the $C_4$–$C_5$ bond, but cyclization to **12** is competitive. The enyne **9** derived from **12** thus represents the interface of two connected energy surfaces (Schemes I and II).

**Acknowledgment** is made to the donors of the Petroleum Research fund, administered by the American Chemical Society, for partial support of this work. We also thank the National Science Foundation (Grants CHE 8011399 and CHE-7916210) for support of this work and of the NSF Northeast Regional NMR Facility at Yale University. M.R.M. and S.E.P. are grateful for fellowships generously provided by the Humphrey Chemical Co. and by the Commonwealth Fund.

**Supplementary Material Available:** Descriptions of isolation, characterization, and independent syntheses of products (2 pages). Ordering information is given on any current masthead page.

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(5) (a) For an excellent review, see: Huntsman, W. D. In "The Chemistry of Ketenes, Allenes, and Related Compounds"; Patai, S., Ed.; Wiley: New York, 1980; Vol. 2, p 522. (b) Huntsman, W. D.; De Boer, J. A.; Woosley, M. H. *J. Am. Chem. Soc.* **1966**, *88*, 5846. (c) Huntsman, W. D.; Dykstra, K. A., unpublished work as cited in ref 5a. (d) Huntsman, W. D.; Dykstra, K. A.; Giannamore, V. P.; Weaver, K. C.; Yin, T. K. 181st National Meeting of the American Chemical Society, Atlanta, GA, March 1981; American Chemical Society: Washington, D. C., 1981; PETR 14.

(6) Although the labeling in **10**-$d_6$ was apparently the same as that which would result from a statistical distribution of *all* the deuteriums, the specificity of the labeling in **10**-$d_1$ (from pyrolysis of **15**) showed that such randomization did not occur.

(7) (a) Precedent exists for the *reverse* of **16** → **17**: Dalacker, V.; Hopf, H. *Tetrahedron Lett.* **1974**, 15. (b) Pyrolysis of the proposed eneallenic intermediate **16** gave **9**, in accord with a previous observation.[5c]

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# Surface Photochemistry: Deviation of the Course of Reaction in Benzoin Ether Photolysis by Adsorption on Silica Gel[1]

Paul de Mayo,* Akira Nakamura, Peter W. K. Tsang, and S. King Wong*

*Photochemistry Unit, Department of Chemistry*
*University of Western Ontario*
*London, Ontario N6A 5B7, Canada*

*Received July 14, 1982*

Recently, we have been concerned to show the occurrence of, and constraints on, movement of closed-shell molecules[2] and radical pairs[3] when adsorbed on silica gel. From these studies it seemed to us that the constraints imposed were such that the reaction course of a photochemical process in solution having important steric demands ought to be capable of profound change when the reactant was adsorbed on a silica gel surface. We report the first clear example of such a major deviation in reaction pathway.

The photolysis of benzoin derivatives in solution has been studied extensively, and the main details of the reaction have been elucidated.[4,5] In the case of benzoin ethers (**1a**,**b**; Scheme I) the reaction proceeds via the triplet and the radical pair (**2**; type I cleavage) to give, as main products, the pinacol ethers (**4**) and benzil (**5**), derived from both geminate pair escape and combination, together with minor amounts of benzaldehyde and benzyl methyl ether. It appeared possible that a silica gel surface might function in two senses: (a) restrict the translational movement in the radical pairs and permit other forms of recombination, for which there is some analogy;[6,7] (b) if the absence of the potentially possible type II hydrogen abstraction (to give **3**) were to be attributed, in part, to the low occupancy by **1** of the necessary cisoid conformation in solution, then hydrogen bonding with the silica gel could produce the required conformation.[9]

Our results in methanolic solution, obtained as controls, and on a silica gel surface are summarized in Table I.[14] In the solution photolysis the previously unreported type II contributes in a minor way and decreases further at lower temperatures. Photolysis on a silica gel surface[15] provided a dramatic difference in behavior.

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(1) Publication No. 285 from the Photochemistry Unit, University of Western Ontario.

(2) Bauer, R. K.; Borenstein, R.; Mayo, P. de; Okada, K.; Rafalska, M.; Ware, W. R.; Wu, K. C. *J. Am. Chem. Soc.* **1982**, *104*, 4635. Mayo, P. de; Okada, K.; Rafalska, M.; Weedon, A. C.; Wong, G. S. K. *J. Chem. Soc., Chem. Commun.* **1981**, 820.

(3) (a) Avnir, D.; Mayo, P. de; Ono, I. *J. Chem. Soc., Chem. Commun.* **1978**, 1109. (b) Avnir, D.; Johnston, L. J.; Mayo, P. de; Wong, S. K. *Ibid*, **1981**, 958. See also: Leffler, J. E.; Zupancic, J. J. *J. Am. Chem. Soc.* **1980**, *102*, 259. Leffler, J. E.; Barbas, J. T. *Ibid.* **1981**, *103* , 7768.

(4) Bak, C.; Praefke, K. *Z. Naturforsch.* **1978**, *33b*, 106. Pappas, S. P.; Chattopadhyag, A. *J. Am. Chem. Soc.* **1973**, *95*, 6484. Lewis, F. D.; Lauterbach, R. T.; Heine, H. G.; Harmann, W.; Rudolph, H. *Ibid.* **1975**, *97*, 1519. Dominh, T. *Ind. Chim. Belg.* **1971**, *36*, 12. Heine, H. G. *Tetrahedron Lett.* **1972**, 4755. Heine, H. G.; Rosenkrantz, H. J.; Rudolph, H. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 974. Ledwith, A.; Russell, P. J.; Sutcliffe, L. H. *J. Chem. Soc., Trans. 2* **1972**, 1925.

(5) Sondner, M. R.; Osborn, C. L. *Tetrahedron Lett.* **1974**, 415.

(6) Turro[8] has reported the formation of minor amounts of *p*-methylphenylacetophenone from the photolysis of dibenzyl ketone in micelles.

(7) We have observed *p*-methylphenylacetophenone formation from the photolysis of dibenzyl ketone on a silica gel surface. (L. J. Johnston, unpublished results from these laboratories).

(8) Turro, N. J.; Chow, M. F.; Chung, C. J.; Kraeutler, B. *J. Am. Chem. Soc.* **1981**, *103*, 3886.

(9) The factors affecting the ratio of type I/type II for phenyl ketones have been discussed from the points of view of rigidity of the structure,[10] stereochemistry,[11a,12] and electronic effects.[11b,13]

(10) Padwa, A. *Acc. Chem. Res.* **1971**, *4*, 48. Padwa, A.; Alexander, E.; Niemcyzk, M. *J. Am. Chem. Soc.* **1969**, *91*, 456.

(11) (a) Wagner, P. J.; Kemppainen, A. E. *J. Am. Chem. Soc.* **1968**, *90*, 5896. (b) Wagner, P. J. *Acc. Chem. Res.* **1971**, *4*, 168.

(12) Yang, N. C.; Dominh, T. *Tetrahedron Lett.* **1966**, 3671. Lewis, F. D.; Hilliard, T. A. *J. Am. Chem. Soc.* **1970**, *92*, 6672.

(13) Turro, N. J.; Lewis, F. D. *J. Am. Chem. Soc.* **1970**, *92*, 311.

(14) Benzaldehyde and benzyl methyl ether were produced in trace amounts.

0002-7863/82/1504-6824$01.25/0